Identification of Non-unitary triplet pairing in a heavy Fermion superconductor UPt$_3$

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A NMR experiment recently done by Tou *et al.* on a heavy Fermion superconductor UPt$_3$ is interpreted in terms of a non-unitary spin-triplet pairing state which we have been advocating. The proposed state successfully explains various aspects of the seemingly complicated Knight shift behaviors probed for major orientations, including a remarkable **d**-vector rotation under weak fields. This entitles UPt$_3$ as the first example that a charged many body system forms a spin-triplet odd-parity pairing at low temperatures and demonstrates unambiguously that the putative spin-orbit coupling in UPt$_3$ is weak.

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Except for the famous example of neutral superfluid Fermion system ^{3}He, no charged Fermion many body system has been known to exhibit spin triplet pairing in nature so far; that is, a triplet superconductor is not firmly identified yet. A heavy Fermion superconductor UPt$_3$ [1] has been regarded as a prime candidate for a triplet superconductor because the observed double transition ($T_{c1} \sim 0.58$K and $T_{c2} \sim 0.53$K) and multiple phases (A, B, and C phases) in H vs T apparently point to some unconventional pairing state where a Cooper pair must have internal degrees of freedom responsible for the multiple phases.

A central controversy in identifying the pairing symmetry in UPt$_3$ lies in whether the internal degrees of freedom as the origin nearly degenerate superconducting transition temperatures come either from the orbital part [2,3] or from the spin part [4] of a Cooper pair. There are the three major scenarios for explaining the multiple phase diagram, apart from the so-called accidental degeneracy scenario [5] whose proposed state is not qualified in detail as yet, being unable to compare it with the above three on an equal footing. The orbital scenarios identify the pairing symmetry as a two-dimensional representation whose multi-dimensionality of the orbital part is responsible for the degeneracy, namely the singlet pairing E$_{1g}$ proposed by Joynt [3], the triplet pairing E$_{2u}$ by Sauls [2]. The latter assumes that the degeneracy is broken by the antiferromagnetism and spin-orbit coupling (SOC) is strong. Thus in E$_{2u}$ the spin of a pair is firmly locked to the crystal lattice. In the spin scenario [4], on the other hand, the degeneracy comes from the spin part of the pair in which weak SOC is assumed by considering that SOC in a one-particle level is already taken account in forming heavily renormalized quasi-particle characteristic of heavy Fermion materials.

It was not an easy task to distinguish the above three scenarios. Since usual thermodynamic or transport measurements extract power low indices in their T-dependence, which reflect the energy gap topology. The accumulated experiments all point to the gap vanishing at both point and line [1]. This is consistent with the above scenarios which yield more or less similar gap topology. An obvious and decisive experiment is to measure the Pauli spin susceptibilities χ_i for the principal orientations ($i = a, b, c$-axes) in the hexagonal crystal since in the singlet E$_{1g}$, χ_i decreases for all directions, and in the triplet E$_{2u}$, χ_a and χ_b (χ_c) remain unchanged (decreases) below T_c, irrespective of the three phases (A, B, and C), that is, the three phases give rise to the identical behavior in their scenarios. In the spin scenario the χ_i behavior is much more subtle and complicated as shown shortly.

Owing to technological developments in making high quality single crystals by Ōnuki group and improvements of NMR instrumentation by Asayama and Kitaoka group, their joint work [6] has culminated in success of measuring the Knight shift (KS) by probing ^{195}Pt nuclear magnetic resonance using single crystals (two crystals: ♯3, ♯4). They extend and refine the previous experiment [7] to much more wider fields and yet unexplored field orientations. The new experiment covers virtually all the phases in H vs T plane for major H orientations, enabling us to completely determine the Cooper pair spin structure.

The purpose of this paper is to demonstrate that a single and simple Ginzburg-Landau (GL) free enegy based on a few basic assumptions can explain all aspects of the seemingly complicated results of their experiment [6] summarized in Table 1, leading us to identify the pairing symmetry in UPt$_3$. Before going into detailed analysis of the Knight shift changes for major orientations, we first reexamine our fundamental assumptions in the light of the new NMR experiment.

The first and most central assumption, that is, the effective SOC felt by Cooper pairs is relatively weak. This implys that under symmetry operations in D$_{6h} \times SO(3) \times \mathcal{T} \times U(1)$ (D$_{6h}$ hexagonal point group, $SO(3)$ spin rotation, $\mathcal{T}$ time reversal and $U(1)$ gauge symmetry) the spin and orbital parts of the spin-triplet order parameter described by $\Delta_{\alpha,\beta}(\mathbf{k}) = i(\sigma \cdot \mathbf{d}(\mathbf{k})\sigma_2)_{\alpha,\beta}$ in terms of the **d**

vector behave independently. The strong SOC assumption adopted by the orbital scenarios, under the symmetry operations the spin and orbital part transform simultaneously and the Cooper pair spin is strongly locked to the crystal lattice and is not rotatable. In this strong SOC case one must resort to the remaining possibility of the orbital part, which is the case in the E_{2u} scenario. Tou's result [6] that the field as low as $H(\parallel \mathbf{c}) \sim 2kG$ makes the Cooper pair spin rotate clearly shows that weak SOC is indeed the case for UPt$_3$. (Note that the BC boundary is far off at $\sim 12kG$.) This is one of the most important significance in their experiment because almost all theories for heavy Fermion superconductors take strong SOC for granted since Anderson's proposal [8].

The second assumption of spin-triplet degeneracy of our pairing function is consistent with Tou' experiment [6] since through their Knight shift change one can estimate the Pauli spin susceptibilities χ_i for various directions coming from the quasi-particles at the Fermi surface. (Don't confuse those with the total bulk susceptibilities which are of course very anisotropic as is well known) According to their data [6], χ_i both parallel and perpendicular to the c-axis are nearly isotropic, supporting the triple degeneracy in spin space and leading to nearly $SO(3)$ symmetry.

The third assumption that the antiferromagnetic (AF) fluctuations characterized by the triple-Q vectors with $\mathbf{Q}_1 = (\frac{1}{2}, 0, 0)$ and its equivalent positions $\mathbf{Q}_2$ and $\mathbf{Q}_3$ in reciprocal space ($a^* = b^* = \frac{4\pi}{a\sqrt{3}}$, $c^* = \frac{2\pi}{c}$) in the hexagonal plane [11] are responsible for breaking the triple degeneracy. This is not inconsistent with their experiment because the static AF order is not present [7]. The triple Q-AF fluctuation structure probed by neutron experiments [9–11] is symmetry-broken from the outset by, for example, the incommensurate lattice modulation whose presence or absence exhibit a good correlation with the double transition [12], leading to a different weight to the triple Q fluctuations. Therefore it is possible to break the hexagonal symmetry by this longitudinal AF fluctuations. Without loosing generality we take $\mathbf{Q}_1 \parallel \mathbf{a}^* \parallel \mathbf{b}$ whose fluctuation is differed from those at $\mathbf{Q}_2$ and $\mathbf{Q}_3$, implying that the symmetry of the hexagonal plane is lowered to two-fold symmetry, which is indeed observed by Tou's experiment [6] as will be seen. They single out the two-fold unique axis in the nominally hexagonal plane. That is remarkable.

Let us now start out by writing down the phenomenological GL free energy, derived based on the above three assumptions:

$$F = \alpha_0(T - T_{c0})|\mathbf{d}|^2 + \frac{1}{2}\beta_1|\mathbf{d}|^4 + \frac{1}{2}\beta_2|\mathbf{d}^2|^2 - \gamma|\mathbf{b}\cdot\mathbf{d}|^2 - \lambda|\mathbf{c}\cdot\mathbf{d}|^2$$

where $\mathbf{Q}_1 \parallel \mathbf{b}$. The last term $\lambda|\mathbf{c}\cdot\mathbf{d}|^2$ which is somewhat ad hoc expresses a weak anisotropy of the order parameter in spin space, reflecting the fact that the Knight shift changes below T$_c$ for $H=2kG$ parallel to the c-axis [6]. This free energy leads to

$$F = \sum_{j=a,b,c} \alpha_0(T - T_c^j)|d_j|^2 + \frac{1}{2}\beta_1|\mathbf{d}|^4 + \frac{1}{2}\beta_2|\mathbf{d}^2|^2$$

with $T_c^b = T_{c0} + \frac{\gamma}{\alpha_0} > T_c^c = T_{c0} + \frac{\lambda}{\alpha_0} > T_c^a$ for $\gamma > \lambda > 0$. The three transition temperatures T_c^a, T_c^b and T_c^c which were originally degenerate are split into the two groups: T_c^b and $\{T_c^a$ and $T_c^c\}$ by the symmetry breaking field as mentioned. The latter two are further assumed to be slightly different $T_c^a < T_c^c$ due to the λ-term because of the small uniaxial anisotropy of the system.

At $T = T_c^b$, which is identified as the upper critical temperature $T_{c1} = 0.58K$ the A phase characterized by $d_a = 0, d_b \neq 0$ and $d_c = 0$ appears first. Then at a lower temperature, $T = T_c^c$ which is identified as $T_{c2} = 0.53K$ the second order transition from the A phase to the B phase characterized by a non-unitary triplet state: $d_a = 0, d_b \neq 0$ and $d_c \neq 0$ takes place where the above free energy leads to the phase difference between d_b and d_c by $\pi/2$ when $\beta_2 > 0$. It can be proved within the above free energy that third transition at $T = T_c^a$, which is designed to situate a few mK below $T = T_c^c$ never realized at zero field.

Let us now discuss the phase diagrams for external field $\mathbf{H}$ applied parallel to and perpendicular to the c-axis. We must take into account the vortex structure based on the above free enegy functional by adding the terms describing the spatially varied order parameter: $F = F_{grad} + F_{bulk}$ with

$$F_{grad} = \sum_{j=a,b,c} \{K_1^j(|D_x d_j|^2 + |D_y d_j|^2) + K_2^j|D_z d_j|^2\}$$

$$F_{bulk} = \sum_{j=a,b,c} \alpha_0(T - T_c^j)|d_j|^2 + \frac{1}{2}\beta_1|\mathbf{d}|^4$$

$$+ \frac{1}{2}\beta_2|\mathbf{d}^2|^2 + \frac{1}{2}\Delta\chi_P|\mathbf{H}\cdot\mathbf{d}|^2.$$

The gradient term F_{grad} describes the spatial variation of the order parameter under external field with the gauge invariant derivative $D_j = -i\hbar\partial_j - \frac{2e}{c}A_j$ ($\mathbf{A}$ is the vector potential). Here there exist two kinds (K_1^j and K_2^j ($j = a, b$ and c) of the gradient term associated with hexagonal symmetry where K_1^b (K_2^b) can differ from K_1^a and K_1^c (K_2^a and K_2^c) because of the symmetry breaking AF fluctuation, that is, $K_1^b = K_1 - \zeta\mathbf{M}^2, K_2^b = K_2 - \zeta'\mathbf{M}^2, K_1^a = K_1 + \zeta\mathbf{M}^2, K_2^a = K_2 + \zeta'\mathbf{M}^2, K_1^c = K_1' + \zeta\mathbf{M}^2, K_2^c = K_2' + \zeta'\mathbf{M}^2$. Here $\mathbf{M}^2$ is the amplitude of the AF fluctuation polarized along the b-axis. It should be noted that

there is no so-called gradient mixing term, which washes out the desired tetra-critical point, in the present spin scenario. This is quite different from that in the orbital scenarios [2,3] where the gradient mixing is inevitable.

The resulting phases in the H vs T shown in Fig.1 are fully characterized by specifying the $\mathbf{d}$ vector in each phase, that is, its direction, the number of the components, and the relative phase. The three vectors in the spin-triplet state are now denoted by the real vectors $\hat{\mathbf{a}}$, $\hat{\mathbf{b}}$ and $\hat{\mathbf{c}}$ referring to the Cartesian coordinate in the hexagonal crystal. The high T and low (high) field A(C) phase is described by a single component $\mathbf{d}$ vector, while the B phase in the low T and low H is a non-unitary state characterized by two-component $\mathbf{d}$ vector whose relative phase is $\frac{\pi}{2}$. Because of the $\Delta\chi_P$ term in the above free energy, which tends to align the $\mathbf{d}$-vector perpendicularly to $\mathbf{H}$, the B phase for $\mathbf{H} \parallel \mathbf{c}$ is further subdivided into $\hat{\mathbf{b}}+i\hat{\mathbf{c}}$ in low H and $\hat{\mathbf{b}}+i\hat{\mathbf{a}}$ in high H. As $H(\parallel \mathbf{c})$ increases the $\mathbf{d}$ vector rotates, corresponding to the KS behavior at $H \sim 2$kG in Table 1.

We analyze the KS experiment by Tou $et\ al.$ [6,7], whose results are summarized in Table I: In the case of $\mathbf{H} \parallel \mathbf{c}$ the KS does not (do) change below T_c for $H \lesssim 2$kG ($H > 3$kG) (see their Fig.4 [6]). This characteristic field H_{rot} differs from that of the BC transition at 12kG, through which KS remains unchanged. According to the above theory within the B phase region $\hat{\mathbf{b}}+i\hat{\mathbf{c}}$ in low H changes into $\hat{\mathbf{b}}+i\hat{\mathbf{a}}$ in high H because the $\mathbf{d}$ vector tends to orient perpendicularly to the field direction, and the BC transition is from $\hat{\mathbf{b}}+i\hat{\mathbf{a}}$ to $\hat{\mathbf{a}}$. Thus KS change does occur at H_{rot}, never at H_{BC}. This is precisely the case seen experimentally. The implication of the $\mathbf{d}$ vector rotation is obvious that SOC to lock the spin to the lattice is not strong, but weak enough to reoriente under a field as low as 2kG.

When $\mathbf{H} \parallel \mathbf{a}$, since both $\hat{\mathbf{b}}+i\hat{\mathbf{c}}$ (B phase) to $\hat{\mathbf{c}}$ (C phase) are perpendicular to H, KS should not change below T_c for any field strengths, even crossing the BC boundary situated at ~ 7kG. This coincides with the observations done for H=11, 4.7, 2.1 and 1.8KG (see their Fig.2 [6]).

As for $\mathbf{H} \parallel \mathbf{b}$, KS should and should not change below T_c for the B phase and C phase respectively. The experiments under H =1.9, 2.4, 3.4, 4.7 and 5.3kG (B phase) and H =8.0 and 9.7kG (C phase) confirm this prediction (see their Fig.3 [6]). This means that the SOC in the basal plane is strong enough not to depin the $\mathbf{d}$ vector parallel to the the b-axis by the field up to $H_{BC} \sim 7$kG. In view of the difference in the characteristic energy scales for $\mathbf{H} \parallel \mathbf{b}$ ($T_c^b - T_c^c \sim 50$mK) and $\mathbf{H} \parallel \mathbf{c}$ ($T_c^c - T_c^a \ll 50$mK), this is understandable.

As pointed out by Tou $et\ al.$ [6], their data allow to draw the information on the A phase, which was quite scarce. By carefully comparing the two lowest field data sets for $H \parallel c$ (their Fig.4) and $H \parallel b$ (their Fig.3) one can clearly see that the decrease of KS does begin to start

at T_{c1} (T_{c2}) for $H \parallel b$ ($H \parallel c$), indicating that in the A phase the $\mathbf{d}$ vector points parallel to the b-axis. This is precisely consistent with our theory.

Importantly enough, the basal plane shows the two-fold symmetry. The $45°$ direction data from the a-axis exhibits an intermediate decrease in the KS change. Theoretically we expect that the decrease in χ corresponds to $\cos^2(\hat{\mathbf{H}} \cdot \hat{\mathbf{d}}) = \frac{1}{2}$.

The absolute values of the KS change ($\sim 0.06\%$ ($\parallel\mathbf{b}$) vs $\sim 0.07\%$ ($\parallel\mathbf{c}$)) which are proportional to the Pauli spin susceptibilities χ_i coming from the quasi-particles near the Fermi surface are roughly isotropic when taking into account the anisotropic hyperfine coupling constants ($\sim 20\%$ difference), supporting the spin space degeneracy scenario (see their detailed analysis [6]). The magnitude of the estimated χ_i is extremely small; only a few $\%$ of the total KS, but Tou's experimental accuracy can sensitively detect it, negating a persistent opinion that the KS measurement is meaningless because the susceptibility is dominated by the T-independent van Vleck term. It is indeed dominated by the van Vleck term, but they are undoubtedly probing the relevant quasi-particle contribution or the Pauli susceptibility part.

An immediate consequence of this identification allows us to determine the direction of the spontaneously induced moment $\mathbf{M}_s$ associated with the non-unitarity in the B phase: $\mathbf{M}_s \propto i\mathbf{d} \times \mathbf{d}^* \parallel \mathbf{a}$ at low fields where $\mathbf{d} = \hat{\mathbf{b}}+i\hat{\mathbf{c}}$. This spontaneous moment $\mathbf{M}_s$ was observed and its magnitude was estimated as ~ 0.5G by μSR experiment [13]. Now the direction of $\mathbf{M}_s$ should be probed. Since macroscopically this moment is cancelled out by the screening surface current and thus the magnetic induction $B = 0$ in the bulk, the unscreened $\mathbf{M}_s$ survives only near the surface whose depth is an order of the penetration length. If the supercurrent whose velocity is v_s (say, 1cm/sec) flows along the c-axis, the electric field $\mathbf{E} = \mathbf{v}_s \times \mathbf{M}_s$ is spontaneously induced transversely, i.e., across the b-axis, whose order of magnitude is estimated as $\sim 10^{-7}$volt/m. This non-trivial prediction should be checked experimentally.

Having analyzed Tou's experiment [6,7], we discuss some of the critiques to our theory in the light of the new findings. The crossing phenomenon of the two upper critical field curves for $H_{c2} \perp \mathbf{c}$ and $\parallel \mathbf{c}$ has been taken as strong evidence that the Pauli limiting is absent (present) for the former (latter), supporting the E$_{2u}$ scenario [14]. Tou's experiment [6,7] shows that this is not the case because both χ's remain unchanged below T_c.

Although we have determined the spin structure of the Cooper pair fairly completely, the precise gap topology remains to be seen. Recent several direction-resolved transport [15] and thermodynamic [16] measurements for each phase should be reexamined in the light of the present theory. We emphasize that the present scenario gives rise to different gap structures for the B, and A

and C phases because the former (latter two) state is non-unitary (unitary), which have distinctively different low enegy excitation spectral structures.

In conclusion, we have identified the spin structures of the Cooper pair in each phase of UPt$_3$, which are fully consistent with the NMR experiment by Tou *et al.* [6]. It is rather self-evident now that since the KS data show at least the four different behaviors for the principal three directions, it is impossible to understand in terms of the two-component pairing state such as the orbital scenarios. The main attractive force for the spin-triplet pairing comes from the paramagnetic fluctuations observed before [17]. The triple degeneracy is weakly broken by the AF fluctuation, resulting in one of the complex **d** vector component locked to the *b*-axis. The fact that the remaining component of the **d** vector is rotatable under weak fields verifies experimentally that the effective spin-orbit coupling felt by Cooper pairs is weak.

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TABLE I. Summary of the Knight shift experiment for the principal directions a, b, and c-axes. $\times$ ($\circ$) denotes the Knight shift unchanges (changes) below T_c.

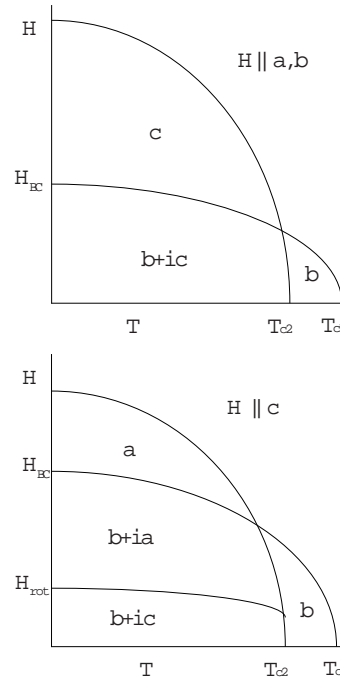|	a	b	c
high field	$\times$	$\times$	$\times$
low field	$\times$	$\bigcirc$	$\bigcirc$

FIG. 1. Schematic phase diagrams in H vs T for $H \parallel a, b$ and $H \parallel c$ where the direction and the components of the **d** vector for each phase are indicated. (H_{BC} the second phase transition between the B and C phases, H_{rot} the rotation field of the **d** vector)